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(54) Process for production of polyfluoroiodide.

(57) A polyfluoroiodide is produced by reacting an acid halide of a polyfluorocarbon in a perhalogenated solvent with I_2 and at least one salt selected from the group consisting of an alkali metal carbonate and an alkaline earth metal carbonate.

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PROCESS FOR PRODUCTION OF POLYFLUOROIODIDE

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to a process for production of polyfluoroiodide.

Polyfluoroiodides are very useful intermediates in producing compounds used as active components of a water-and oil-repellent, a mold-release agent, a finish and so on through telomerization or epoxidation of an olefinic compound with the use of a peroxide.

Description of the Related Art

In order to iodinate a fluorine-containing organic acid, for example, a process comprising forming a silver salt of said organic acid with for example a silver oxide and subsequently reacting the salt with iodine (U.S. Patent No. 2,170,181, the Hunsdiecker reaction) and a process comprising reacting an alkali metal salt of the organic acid with iodine (G.B. Patent Application No. 86134) are proposed. However, in any process, there are some defects such that a reacting agent is expensive, building an apparatus in a commercial scale is difficult, or a yield is not satisfactory.

SUMMARY OF THE INVENTION

It is, therefore, an object of the present invention to provide a process for commercially effective production of an iodine terminated compound which is a valuable intermediate in the fluorine chemical industry due to its specific reactivity.

According to the present invention, there is provided a process for production of a polyfluoroiodide, which process comprises reacting an acid halide of a polyfluorocarbon in a perhalogenated solvent with I_2 and at least one salt, preferably carbonate selected from the group consisting of an alkali metal carbonate and an alkaline earth metal carbonate.

DETAILED DESCRIPTION OF THE INVENTION

The reaction of the present invention cannot be performed in an apparatus made of a conventional metal since iodine is used and the reaction proceeds at relatively high temperature. Then, it is preferable to perform the present reaction in a reactor made of glass under atmospheric pressure.

The reasons why the present reaction is performed in the presence of the perhalogenated solvent are as follows:

In the present reaction, the reaction temperature is raised to around a decomposition temperature of the metal salt such as carbonate. At such the temperature, iodine sublimates. Then, not only iodine tends to block a line of the reaction system, but also a large amount of excess iodine should be used. In addition, when any hydrogen atom is contained in the solvent compound, a hydrogen terminated compound instead of an iodine terminated one may be formed. Also, in the presence of water, a hydrogenated compound may be produced. By selection of the suitable perhalogenated solvent having a suitable boiling point, the reaction temperature can be kept constant, the blockage due to sublimation and the subsequent solidification of iodine can be prevented with reflux of the solvent, and the production of the hydrogen terminated compound can be prevented.

The boiling point of the perhalogenated solvent is usually in the range of from 180 to 260 °C and preferably in the range of from 200 to 240 °C. The preferable perhalogenated solvents are, for example, perchlorobutadiene, perfluoropolyether oil, a solvent for VPS (Vapor Phase Soldering) and so on. In particular, perchlorobutadiene is preferable due to large solubility of I_2 therein. When an amount of perchlorobutadiene is increased, a higher yield can be achieved even when the excessive amount of iodine is in the range of from 1.1 to 2.0 times the stoichiometric amount of iodine.

The reaction temperature depends on the solvent. Usually it is in the range of from 180 to 260 °C and preferably in the range of from 200 to 240 °C.

From the point of the decomposition temperature, a potassium carbonate is particularly preferred.

An amount of the carbonate to be used is from 1.1 to 10 times by molar and preferably from 1.5 to 5 times by molar relative to the acid halide as the starting material.

The reasons why the acid halide is used as a starting material are as follows: When a carboxylic acid is used, water is produced and the yield is decreased. Further, it is very difficult to remove water from the formed salt.

During the present reaction, an acid fluoride of the decomposed product is by-produced, which can be again reacted with iodine and the carbonate to produce the iodine terminated compound substantially stoichiometrically.

The acid halide of the polyfluorocarbon is a compound of the formula:

RfCFXCOF

wherein Rf is a perfluoroalkyl or polyfluoropolyether group and X is fluorine or trifluoromethyl group.

In particular, the process according to the present invention is suitable for the production of the polyfluoroiodide from the acid halide of the polyfluoropolyether.

The polyfluoropolyether is a compound which has a acid halide group(s) at one end or both ends and which has a polymer chain comprising repeating units of the formulas:

$-(CH_2CF_2CF_2O)_a-$, $-(CHClCF_2CF_2O)_b-$, $-(CCl_2CF_2CF_2O)_c-$, $-(CHFCF_2CF_2O)_d-$, $-(CFClCF_2CF_2O)_e-$ and $-(CF_2CF_2CF_2O)_f-$

wherein a, b, c, d, e and f are 0 or a positive integer, and satisfy inequalities of $2 \leq a+b+c+d+e+f \leq 200$ and $1 \leq a+c+d+f$, respectively.

Further, the polyfluoropolyether may be a compound, for example Krytox (trade mark) available from Du Pont, comprising a repeating unit of the formula:

$$-(\underset{\displaystyle CF_3}{\overset{}{C}}FCF_2O)-$$

$$-(\overset{CF_3}{\overset{|}{C}}FCF_2O)-$$

and a compound, for example Fomblin (trade mark) available from Montefluos, comprising a repeating unit of the formula:

$$-(\overset{CF_3}{\overset{|}{C}}FCF_2O)_p-(CF_2O)_q-(\overset{CF_3}{\overset{|}{C}}FO)_r-$$

wherein p, q and r satisfy an inequality of $2 \leq p+q+r \leq 200$.

The reaction of the present invention proceeds according to the reaction equations as follows:

$$RfCFXCOF + MCO_3 \rightarrow RfCFXCOOM + CO_2 + MF$$

$$RfCFXCOOM + I_2 \rightarrow RfCFXI + CO_2 + MI$$

According to the present invention, it is possible to produce the iodide commercially through only one pot reaction under atmospheric pressure in the glass reactor without corrosion.

With the perhalogenated solvent having a suitable boiling point, the reaction temperature can be kept constant. With the reflux of the solvent, the blockage due to solidification of iodine may be prevented. Further, the production of the hydrogen terminated compound may be prevented.

With the use of an excess amount of the carbonate of the alkali metal or the alkaline earth metal relative to the acid halide, the production of the hydrogen terminated compound or the acid fluoride is prevented to increase the yield of the desired polyfluoroiodide.

The present invention will be hereinafter explained further in detail by following examples.

Example 1

Twenty ml of well dried hexachloro-1,3-butadiene, 0.6 gram of potassium carbonate powder (4.4 millimole) and 3.3 grams of iodine (13 millimole) were supplied in a 100 ml four necked flask in a stream of nitrogen and then heated to 200 °C with stirring. Then, 12 grams of the acid fluoride of the perfluoropolyether of the formula:

$F(CF_2CF_2CF_2O)_n-CF_2CF_2COF$

wherein n is 34 on the average (2.1 millimole) was dropwise added into the flask. After the addition of the acid fluoride, the mixture was heated at reflux at 210 to 220 °C.

After 7 hours, the reaction solution was analyzed with an infrared spectrometer and the chart from the infrared spectrometer showed absorption due to the carbonyl group disappeared but absorption due to the C-I bonds appeared at 910 cm^{-1}.

After the reaction mixture was recovered from the flask and filtered, the solvent was removed with a separatory funnel and dried off under vacuum to obtain 12.1 grams of the product. In the NMR and IR analyses, any impurity (a carboxylic acid terminated compound, an acid fluoride or a hydrogen terminated compound) was not detected, and the iodine terminated compound was detected.

Example 2

In 150 ml of hexafluoro-1,3-butadiene in a 500 ml four necked flask, 12.0 grams of potassium carbonate powder (8.7×10^{-2} mole) and 52 grams of iodine (0.2 mole) were dispensed in a stream of nitrogen. Then, 120 grams of the acid fluoride of the formula:

$[-CF_2CF_2CF_2O-(CF_2CF_2CF_2O)_n-CF_2CF_2COF]_2$

wherein n is 10 on the average (0.03 mole) was dropwise added while the temperature of the mixture was kept at 210 to 220 °C. After six hours, disappearance of absorption due to the carbonyl group in the IR chart was confirmed. Then, the reaction solution was purified as in Example 1 to obtain 120 grams of the product. The yield was 95 %. The product was identified to be a compound of the formula:

$[-CF_2CF_2CF_2O-(CF_2CF_2CF_2O)_n-CF_2CF_2I]_2$

Example 3

In a 100 ml four necked flask, 24 ml of hexachloro-1,3-butadiene and 2.49 grams of iodine (9.84×10^{-3} mole) were charged in a stream of nitrogen and mixed to obtain a solution. Then, 0.68 gram of potassium carbonate (4.92×10^{-3} mole) was added to the solution and heated to 210 °C.

Then, 12 grams of the perfluoropolyether of the formula:

$F-(CF_2CF_2CF_2O)_n-CF_2CF_2COF$

wherein n is 21 (3.28×10^{-3} mole) was dropwise added into the flask. After the dropping, the mixture was further heated at reflux. After about seven hours, the reaction solution was analyzed with IR and it was confirmed that there is no absorption due to the carbonyl group in the chart. The reaction solution was purified as in Example 1 to obtain 12.1 grams of the product. The yield was 98 %. When analyzed with IR and NMR, it is identified that the iodine terminated compound was stoichiometrically produced.

Claims

1. A process for production of a polyfluoroiodide, which process comprises reacting an acid halide of a polyfluorocarbon in a perhalogenated solvent with I_2 and at least one salt selected from the group consisting of an alkali metal carbonate and an alkaline earth metal carbonate.

2. The process according to claim 1 in which the polyfluorocarbon is a polyfluoropolyether.

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EUROPEAN SEARCH REPORT

Application Number

EP 89 11 1784

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
A	J. MARCH "ADVANCED ORGANIC CHEMISTRY" 2nd edition, 1977 * page 668, chapter 4-39 - page 669 *	1	C 08 G 65/00 C 08 F 8/22 C 07 B 39/00
A	US-A-3 505 411 (D. RICE et al.) * claim; column 2, lines 30-40 *	1,2	
P,A	EP-A-0 272 698 (DAIKIN) * claims 4,5 *	1,2	
P,A	EP-A-0 293 884 (DAIKIN) * page 4, lines 1-30 *	1,2	

TECHNICAL FIELDS SEARCHED (Int. Cl.5)

C 08 G
C 08 F
C 07 B

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
Berlin	05 November 90	BOEKER R.B.

CATEGORY OF CITED DOCUMENTS

X: particularly relevant if taken alone
Y: particularly relevant if combined with another document of the same category
A: technological background
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